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(58) Field of search

C7A

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**(54) Silver-copper-germanium Alloys
Having High Oxidation Resistant
Melts**

**(57) A silver-copper-germanium base
alloy is disclosed consisting by weight
of 40 to 85% silver, 15 to 60% copper
and 0.1 to 10% germanium.**

Optionally, up to 15% by weight of

**the base alloy may be replaced with
tin and up to 10% by weight of at least
one of gold, palladium and platinum.
The presence of germanium in the
alloy virtually eliminates oxidation of
the melt during the melting and
casting of the alloy and thereby also
improves resistance to tarnishing
when the alloy is used in an oral
environment.**

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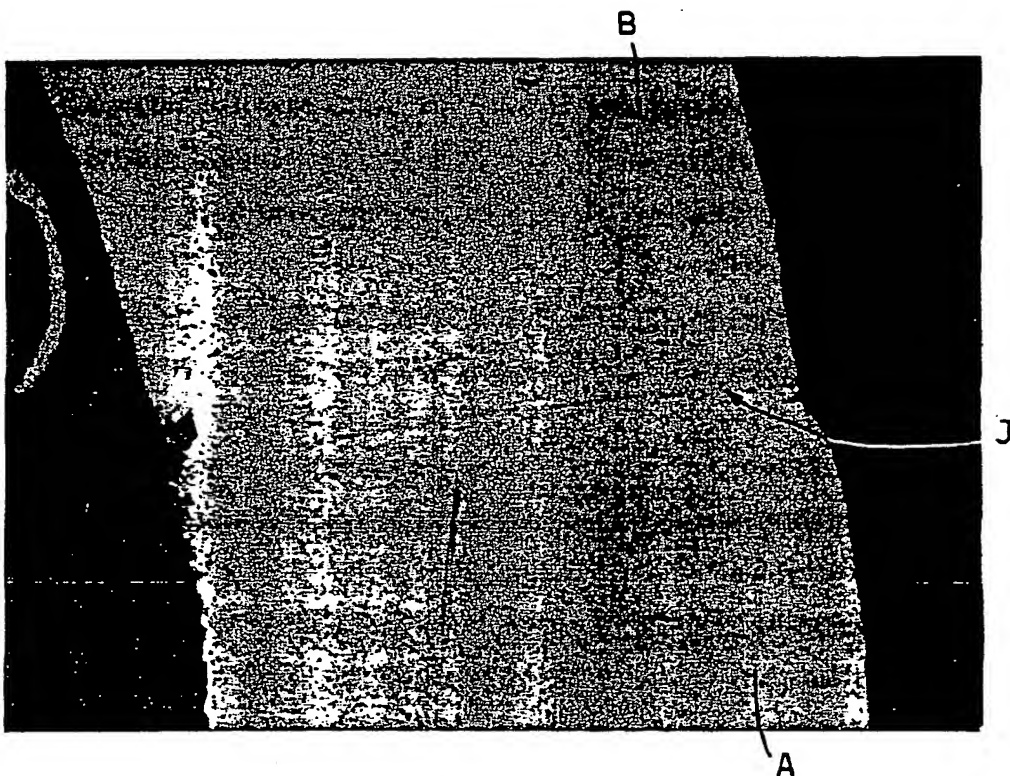
<p>(21) Application No 9423165.1</p> <p>(22) Date of Filing 17.11.1994</p> <p>(30) Priority Data (31) 9323787 (32) 18.11.1993 (33) GB</p>	<p>(51) INT CL⁶ B23K 20/00 35/00</p> <p>(52) UK CL (Edition N) B3R RPM R120 R71470 R71473 R71492 C7A AB23X AB23Y AB279 AB289 AB309 AB319 AB32Y AB320 AB325 AB327 AB329 AB33X AB331 AB333 AB335 AB337 AB339 AB349 AB369 AB389 AB399 AB419 AB439 AB459 AB489 AB519 AB539 AB549 AB559 AB610 AB613 AB618 AB619 AB62X AB621 AB624 AB627 AB630 AB635 AB66Y AB661 AB663 AB665 AB667 AB689 AB670 AB675 AB680 AB684 AB686 AB688 AB70X AB702 A711</p> <p>(56) Documents Cited GB 0925182 A EP 0248914 A</p> <p>(58) Field of Search UK CL (Edition N) B3R, C7A INT CL⁶ B23K Online WPI</p>
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(54) Diffusion bonding process using silver/germanium alloys and a silver germanium alloy for use in the method

(57) A method of joining two elements uses a silver based alloy having a germanium content, which method comprises the steps of: providing two elements to be joined together, at least one of the elements comprising a silver based alloy having a germanium content; placing the two elements adjacent one another such that a portion of a free surface of the silver based alloy contacts a portion of a free surface of the other element without interposing a filler material between the two free surfaces; and heating the two free surfaces where the two elements are adjacent one another to a temperature below that of the melting temperatures of any of the constituent materials of the elements thereby joining the two elements by a diffusion process. A silver/germanium alloy suitable for use in the method has a silver content of at least 77% by weight and a germanium content of between 0.4 and 7% by weight, which alloy contains boron as a grain refiner at a concentration of less than 20 parts per million. The remainder of the alloy is copper.

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PATENTS ACT 1977

"A method of joining materials together by a diffusion process using silver/germanium alloys and a silver/germanium alloy for use in the method"

The present invention relates to a method of joining metals together by a diffusion process using silver/germanium alloy and to a silver/germanium alloy composition which is particularly suitable for use in the method of the invention. More particularly, the present invention relates to such a method using a copper/silver/germanium alloy which does not require the introduction of an additional filler material.

Conventionally, metals are joined by three principle methods: welding, brazing and soldering. When welding using a filler, a filler material is chosen which has a composition which is similar to the two parts being joined and the actual contact regions of the adjacent metal parts are melted to effect the join. When resistance welding or laser welding, e.g. spot welding, the adjacent metal parts to be joined are raised to a high temperature and melted, no filler metal being required to effect the join. When brazing or soldering, a filler metal is used which has an appreciably lower melting point than that of the two parts being joined such that the contact regions of the metal parts being joined are not melted. Typically, solders melt below about 450°C whereas brazing uses filler metals of greater strength which have a melting temperature of greater than 450°C. These methods all require either the use of a filler metal which forms a liquid phase upon heating to facilitate the joining of the parts or the

melting of the adjacent metal parts to be joined. The filler metal or the melted parts of the metals to be joined then cools and solidifies thereby creating a bond at the molecular level.

Silver and silver alloys have conventionally been joined using a brazing process. However, so-called "fire staining" occurs at the high temperatures required to effect a bond using brazing techniques.

Because of its high thermal and electrical conductivity silver and silver based alloys are well known for their use in electrical and electronic contacts. Silver is also a precious metal and is used in the manufacture of jewellery and silverware. Accordingly, it becomes necessary to create bonds between both silver and silver alloys and other metals whether they are ferrous or non-ferrous. It is also desirable to bond ceramics or plastics to metals. This has largely been done in the past by tack welding, soldering or brazing the joints together which introduces impurities from the fluxing agent or solder into the silver/silver alloy.

A fire stain or fire spot is caused by the oxidation of the copper at high temperatures. Additionally, it is well known that silver tarnishes easily. This is because the silver, which does not readily oxidise at ambient temperatures, reacts with sulphur or hydrogen sulphide to cause the familiar tarnishing effect. It is known that the addition of a small quantity of germanium to a silver/copper alloy slows down the rate at which the silver reacts with sulphur and hydrogen sulphide

thus reducing the tarnishing effect as well as reducing fire stain when the silver/copper/germanium alloy is heated to high temperatures at which the copper would normally oxidise.

It is possible to braze or flame anneal in air a silver/copper/germanium ternary alloy, without causing the production of fire stain and to provide a finished product which is less susceptible to tarnishing. However, a filler metal is required to perform the brazing to create a bond or joint and it is also necessary to raise the temperature of the silver alloy being worked to a high temperature, thus producing large temperature gradients in a bond area.

It is an object of the present invention to provide a method of joining metals without needing to provide an additional filler metal. It is another object of the present invention to provide a method of joining metals at temperatures below the solidus temperature of the constituent materials of the parts being joined. It is a further object of the invention to provide a silver/germanium alloy which is particularly suited to joining by the method of the invention or by non-filler welding techniques.

Accordingly, in one aspect, the present invention provides a method of joining two elements using a silver based alloy having a germanium content, which method comprises the steps of: providing two elements to be joined together, at least one of the elements comprising a silver based alloy having a germanium content; placing the two elements adjacent one another such that a portion of a free surface of the silver based alloy contacts a portion of a free surface of the other element without interposing a filler material between the two free surfaces; and heating

the two free surfaces where the two elements are adjacent one another to a temperature below that of the melting temperatures of any of the constituent materials of the element thereby joining the two elements by a diffusion process.

In another aspect, the present invention provides a silver/germanium alloy having a silver content of at least 77% by weight and a germanium content of between 0.4 and 7% by weight, which alloy contains boron as a grain refiner at a concentration of less than 20 parts per million.

In order that the present invention may be more readily understood, it will now be described with reference to the accompanying figure, in which there is illustrated a cross-sectional representation through two metal parts A,B joined using a method according to the present invention.

Whilst it is known to be possible to braze a silver/copper/germanium alloy with less risk of fire staining the brazed areas, it has now been found that, surprisingly, it is in fact not necessary to braze such silver/copper/germanium alloy to produce a bond. Accordingly, in producing a joint using a method according to the present invention it is no longer necessary to melt the areas of the join or a filler metal or, indeed, to provide a filler metal at all.

To produce such a joint or bond in accordance with one aspect of the present invention, the following steps are carried out.

The surfaces of the two pieces of material, one of which is a silver alloy containing copper and germanium, are prepared so that the surfaces to be joined (mating surfaces) do not have any large gaps between them such that the two mating surfaces are engaged over the largest possible surface area. The two pieces of material A,B (see the figure) are then placed adjacent one another so that the desired physical arrangement of the joint is achieved. With the pieces of material in this position, heat energy is then applied to the joint J (see figure) to cause diffusion between the adjacent mating surfaces. Heat energy is applied for a pre-determined amount of time such that the temperature of the two pieces of material being joined does not exceed the solidus temperature of any one of the constituents of the two pieces of material. Accordingly, there is no melting of the two pieces of material being joined or bonded and no filler metal is required.

As can be seen from the accompanying figure, the grain structure of both materials A,B in the joint area is substantially unaffected and the join line J is only detectable with difficulty. Thus, such joins are aesthetically pleasing, which is beneficial in jewellery applications.

The ability to form a joint using a silver/copper/germanium alloy in accordance with the present invention is thought to be due to the diffusional motion of the atoms on the mating surfaces of the two pieces of material being joined and, in particular, the bulk diffusion of the germanium atoms into vacancies on the adjacent surface of the other piece of material. Such vacancies are common on the free surfaces of metals and it is therefore possible to join, for example, a metal part

comprising a silver/copper/germanium alloy to either another silver/copper/germanium alloy or to a ferrous or non-ferrous metal with the introduction of an additional filler metal. Additionally as such vacancies may also be present in free surfaces of ceramics or other non-metallic materials such as plastics, it is also possible to join the silver/copper/germanium alloy to non-metallic materials.

All types of joint may be produced using the above described method such as butt or lap type joints.

In one embodiment of the invention the silver/copper/germanium alloy is applied as either a powder, plating or a thin coating to one of the elements to be joined. In this case the silver/copper/germanium alloy, in whatever form, bonds as a separate element to each of the two elements to be joined.

In accordance with the invention a silver/copper/germanium alloy powder may be bonded to another element as a means of providing a silver/copper/germanium coating or plating.

It is also possible using the above described method to produce a multi-layer composite material formed by bonding the silver/copper/germanium alloy to layers of other material, such as other metals, ceramics or plastics as required.

The above described method can be carried out at temperatures as low as 500°C thereby obviating the need for expensive autoclave units or ovens. Joints have been achieved by maintaining the materials to be joined at this temperature for a period of minutes.

In one embodiment of the present invention the silver/germanium alloy comprises a silver content of at least 77% by weight and the germanium content comprises between 0.4 and 7% by weight, the remainder principally being copper apart from any impurities.

In a preferred embodiment of the present invention the silver/germanium alloy comprises a silver content of at least 92.5% by weight and the germanium content comprises between 0.5 and 3% by weight, the remainder principally being copper apart from any impurities.

A silver/germanium alloy which is particularly suitable for use in the method of the present invention, but which also lends itself to joining by resistance welding and laser welding techniques, comprises a silver content of at least 92.5% and a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contains boron as a grain refiner at a concentration of less than 20 parts per million. Thus, it has been found that, remarkably, such low concentrations of boron provide excellent grain refining in a silver/germanium alloy. Indeed, a concentration of less than 10 parts per million and as low as 2 or even 0.9 parts per million is effective for this purpose, imparting greater strength and ductility to the alloy compared with a silver/germanium alloy without a boron content and permitting strong and aesthetically pleasing joints to be obtained using a method embodying the invention or resistance and laser welding techniques.

The silver/germanium alloy of the present invention is resistant to fire stain and no surface pitting of samples was observed after repeated heating (three times)

to temperatures of which the copper/germanium eutectic in known silver/copper/germanium alloys would normally melt and cause pitting.

The boron in a silver/germanium alloy embodying the invention appears to inhibit grain growth even at temperatures used for soldering in the jewellery trade.

Other preferred embodiments of the silver/germanium alloy according to the present invention comprise a silver content of at least 80% or at least 83%.

CLAIMS:

1. A method of joining two elements using a silver based alloy having a germanium content, which method comprises the steps of: providing two elements to be joined together, at least one of the elements comprising a silver based alloy having a germanium content; placing the two elements adjacent one another such that a portion of a free surface of the silver based alloy contacts a portion of a free surface of the other element without interposing a filler material between the two free surfaces; and heating the two free surfaces where the two elements are adjacent one another to a temperature below that of the melting temperatures of any one of the constituent materials of the elements thereby joining the two elements by a diffusion process.
2. A method according to Claim 1, wherein the silver/germanium alloy comprises a silver content of at least 77% by weight and the germanium content comprises between 0.4 and 7% by weight, the remainder principally being copper apart from any impurities.
3. A method according to Claim 2, wherein the germanium content comprises between 0.5 and 3% by weight.
4. A method according to any preceding claim, wherein both elements to be joined comprise the silver/germanium alloy.
5. A method according to any preceding claim, wherein the two adjacent free surfaces of the elements are heated to as low as a temperature of 500°C.

6. A method according to any preceding claim, wherein the element comprising a silver based alloy having a germanium content is a powder, plating or a thin coating.

7. A method according to any preceding claim when used in the manufacture of items of jewellery, silverware or electrical or electronic contacts, or aerospace materials.

8. A method according to any preceding claim, wherein a plurality of superimposed elements are joined together to create a multi-layered product.

9.. A method of joining two elements using a silver based alloy having a germanium content substantially as hereinbefore described.

10. A silver/germanium alloy having a silver content of at least 77% by weight and a germanium content of between 0.4 and 7% by weight, which alloy contains boron as a grain refiner at a concentration of less than 20 parts per million.

11. A silver/germanium alloy having a silver content of at least 77% by weight, a germanium content of between 0.4 and 7% by weight, the remainder being copper apart from any impurities, which alloy contains boron as a grain refiner at a concentration of less than 20 parts per million.

12. An alloy according to Claim 10 or 11, wherein the germanium content comprises between 0.5 and 3% by weight.

13. An alloy according to any one of Claims 10 to 12, wherein the boron content is less than 10 parts per million.

14. An alloy according to Claim 13, wherein the boron content is 0.9 parts per million.

15. Any novel feature or combination of features disclosed herein.

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Examiner's report to the Comptroller under Section 17
(The Search report)

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Relevant Technical Fields

UK Cl (Ed.N) B3R
(ii) Int Cl (Ed.6) B23K

Search Examiner
D N P BUTTERS

Date of completion of Search
19 JANUARY 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
1 TO 9

(ii) ONLINE DATABASE - WPI

Categories of documents

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| <p>X: Document indicating lack of novelty or of inventive step.</p> <p>Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p>A: Document indicating technological background and/or state of the art.</p> | <p>P: Document published on or after the declared priority date but before the filing date of the present application.</p> <p>E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p>&: Member of the same patent family; corresponding document.</p> |
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Category	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

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